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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <p>(54) Title: <b>LAUNDRY ADDITIVES COMPRISING ENCAPSULATED PERFUMES AND MODIFIED POLYESTERS</b></p> <p>(57) Abstract</p> <p>The present invention relates to laundry detergent composition or component compositions comprising encapsulated perfumes and certain modified polyesters. The modified polyesters are also useful as soil release polymers.</p>   |           |  |

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**LAUNDRY ADDITIVES COMPRISING ENCAPSULATED  
PERFUMES AND MODIFIED POLYESTERS**

**Technical Field**

This invention relates to laundry detergent components and compositions containing encapsulated perfumes. More particularly, this invention relates to laundry detergent components and compositions containing modified soil-release polymers and having enhanced perfume impact through encapsulated perfumes.

**Background**

The voluminous prior art relating to detergency in general and perfume delivery in particular shows that numerous attempts have been made to design perfume carrier systems which would allow delivering the perfume to the fabrics; in these attempts, the main goal was to achieve delivery of undiluted, undissipated and unaltered perfume to the fabrics,

so that the perfume would be released at the end of or after the laundry process.

Problems of this nature have been solved by the use of encapsulation technology. Examples are microcapsules such as disclosed in US 4,145,184; US 4,234,627; US 4,446,032; US 3,971,852.

It is equally well recognized that quite an amount of the perfume is wasted or lost during the wash process due to the incomplete deposition of the perfumes onto the fabrics.

One reason for the incomplete or altered deposition of perfume has found to be the negative interaction of soil release polymers. Said polymers are used to enhance cleaning ability of detergents. During the laundering operation, these soil release polymers deposit onto the surface of fabrics immersed in the wash solution. The deposited polymers then form a film which remains on the fabric after it is removed from the wash solution and dried. So far it was therefore necessary to limit the level of soil release polymers in order to achieve an efficient perfume delivery onto the fabrics.

It has now been surprisingly found that certain modified polyesters, as described, for example, in EPA 311 342 are fully compatible with encapsulated perfumes. This finding allows to formulate laundry additives which exhibit better cleaning performance due to the higher levels of polymers now affordable, and in better perfume impact, due to the increased or better deposition of the perfume. According to another embodiment of the present invention, detergent compositions comprising said laundry components and softening clay are also provided.

#### Summary of the invention

The present invention relates to laundry detergent composition or component compositions comprising encapsulated perfumes and certain modified polyesters.

Detailed description of the inventionThe modified polyesters

Modified polyesters herein are substantially linear end-capped esters having molecular weight ranging from about 500, to about 20,000, preferably from about 500 to about 8,000; said ester consisting essentially of, on a molar basis :

- i) from about 1 to about 2 moles of two or more types of end-capping units selected from the group consisting of :
  - a) ethoxylated or propoxylated hydroxy-ethane and propanesulfonate end-capping units of the formula  $(\text{MO}_3\text{S})(\text{CH}_2)_m(\text{CH}_2\text{CH}_2\text{O})(\text{RO})_n-$ , wherein M is a salt-forming cation such as sodium or tetraalkylammonium, R is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 0 to 4;
  - b) sulfoaroyl units of the formula  $-(\text{O})\text{C}(\text{C}_6\text{H}_4)(\text{SO}_3\text{M})$ , wherein M is a salt forming cation;
  - c) modified poly(oxyethylene)oxy monoalkyl ether units of the formula  $\text{XO}(\text{CH}_2\text{CH}_2\text{O})_k-$ , wherein X contains from about 1 to about 4 carbon atoms and k is from about 1 to 100; and
  - d) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula  $\text{NaO}_3\text{S}(\text{C}_6\text{H}_4)-(\text{RO})_n-$ , wherein n is from 1 to 5 and R is ethylene or propylene or a mixture thereof;
- ii) from about 0.5 to about 66 moles of units selected from the group consisting of :
  - a). oxyethyleneoxy units;
  - b) oxy-1,2-propyleneoxy units; and
  - c) mixtures of a) and b);
- iii) from about 1.5 to about 40 moles of terephthaloyl units; and optionally

- iv) from 0 to about 26 moles of 5-sulfoisphtholoyl units of the formula  $-(O)C(C_6H_3)(SO_3M)C(O)-$ , wherein M is a salt forming cation such as an alkali metal or tetraalkylammonium ion.

These polyesters are described in the Applicants copending application USSN 08/088705.

Preferred polyesters herein are random copolymers of dimethyl terephthalate, dimethyl sulfoisophtalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target being to obtain is a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

Most preferred polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol, about 13% by weight of dimethyl sulfobenzoid acid and about 15% by weight of sulfoisophtalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

#### Encapsulated perfumes

The encapsulated perfumes comprise perfume dispersed in certain carrier materials.

In the context of this specification, the term "perfume" means any odoriferous material or any material which acts as a malodor counteractant. In general, such materials are characterized by a vapor pressure greater than atmospheric

pressure at ambient temperatures. The perfume or deodorant materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various tamphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor.

Perfumes which are normally solid can also be employed in the present invention. These may be admixed with a liquefying agent such as a solvent prior to incorporation into the particles, or may be simply melted and incorporated, as long as the perfume would not sublime or decompose upon heating.

The invention also encompasses the use of materials which act as malodor counteractants. These materials, although termed "perfumes" hereinafter, may not themselves have a discernible odor but can conceal or reduce any unpleasant odors. Examples of suitable malodor counteractants are disclosed in U.S. Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

A wide variety of capsules exist which will allow for delivery of perfume effect at various times in the cleaning or conditioning process. The less protection provided results in greater perfume effect in product or washing/conditioning process. More protection results in greater perfume effect during the drying process or even later, after the surface has been treated.

Examples of such capsules with different encapsulated materials are capsules provided by microencapsulation. Here



the perfume comprises a capsule core which is coated completely with a material which may be polymeric. U.S. Patent 4,145,184, Brain et al, issued March 20, 1979, and U.S. Patent 4,234,627, Schilling, issued November 18, 1980, teach using a tough coating material which essentially prohibits the diffusions out of the perfume. The perfume is delivered to fabric via the microcapsules and is then released by rupture of the microcapsules such as would occur with manipulation of the fabric.

Another method involves providing protection of perfume through the wash cycle and release of perfume in the heat-elevated conditions of the dryer. U.S. Patent 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents to textiles through the wash and dry cycle via particles containing hydrogenated castor oil and a fatty quaternary ammonium salt. Perfume may be incorporated into these particles.

U.S. Patent 4,152,272, Young, teaches incorporating perfume into wax particles to protect the perfume through storage in dry compositions and enhance the deposition of the particles on the fabrics during the rinse by the concomitant use of a cationic surfactant. The perfume then diffuses through the wax matrix of the particles on the fabric in the heat-elevated conditions of the dryer.

Greater protection can be provided by choice of encapsulating material to be used to form the capsules, ratio of perfume to encapsulation or agglomeration of particles.

The choice of encapsulated material to be used in the perfume particles of the present invention will depend to some degree on the particular perfume to be used. Some perfumes will require a greater amount of protection than others and the encapsulating material to be used therewith can be chosen accordingly.

In general, the encapsulating materials of the perfumed particles can be a water-insoluble or water-soluble encapsulating material.

Nonlimiting examples of useful water-insoluble materials include polyethylenes, polyamides, polystyrenes, polyisoprenes, polycarbonates, polyesters, polyacrylates, vinyl polymers and polyurethanes and mixtures thereof.

Nonlimiting examples of suitable water-soluble coating materials include such substances as methyl cellulose, maltodextrin and gelatin. Such coatings can comprise from about 1% to about 25% by weight of the particles.

Especially suitable water soluble encapsulating materials are capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble or water dispersible encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials are N-Lok ®, manufactured by National Starch, Narlex ® (ST and ST2), and Capsul E ®. These encapsulating materials comprise pregelatinised waxy maize starch and, optionally, glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Water-soluble encapsulating materials are especially suitable when perfume has to be incorporated into a dry granular or powder product. Such a water-soluble capsule will then protect perfume during storage in product from other conventional laundry composition compounds such as bleach, enzymes and clay.

For enhanced protection of the perfume particles in a liquid product, it is more desirable to encapsulate the perfume with a material that is pH sensitive, i.e., a material that will remain as a coating on the particle in one pH environment but which would be removed from the particle in a different pH environment. For example, such a material could be used to encapsulate the perfume in a liquid fabric softening composition having a pH of about 3. When such a composition is added to the laundry wash water where the pH is greater than 6, the coating material could be stripped away. This would allow for further protection of perfume in liquid compositions over long storage periods, i.e., the perfume would not diffuse out of the particle in the liquid medium as readily. Diffusion of the perfume out of the stripped particle would then take place after the particles were brought into contact with a different pH environment.

The perfume may also be encapsulated with a material that makes the particles more substantive to the surface being treated for example, fabric in the laundry process. Such materials help to deliver the particles to the fabric and maximize perfume release directly on the fabric. Generally, these materials are water-insoluble cationic materials. Examples of useful material include any of the cationic (including imidazolinium) compounds listed in U.S. Patent 3,686,025, Morton, issued August 22, 1972, incorporated herein by reference. Such materials are well known in the art and include, for example, the quaternary ammonium salts having at least one, preferably two, C<sub>10</sub>-C<sub>20</sub> fatty alkyl substituent groups; alkyl imidazolinium salts wherein at least one alkyl group contains a C<sub>8</sub>-C<sub>25</sub> carbon "chain"; the C<sub>12</sub>-C<sub>20</sub> alkyl pyridinium salts, and the like.

Alternative materials useful for encapsulating materials to make them more fabric substantive are described in U.S. Patent 4,234,627, Schilling, issued November 18, 1980, herein incorporated by reference.

The encapsulated perfume particles can be made by mixing the perfume with the encapsulating matrix by spray-drying emulsions containing the encapsulating material and the perfume. In addition, the particle size of the product from the spray-drying tower can be modified. These modifications can comprise specific processing steps such as post-tower agglomeration steps (e.g. fluidised bed) for enlarging the particle size and/or processing steps wherein the surface properties of the encapsulates are modified, e.g. dusting with hydrophobic silica in order to reduce the hygroscopicity of the encapsulates.

A particularly preferred encapsulation process is an emulsification process followed by spray-drying and finally dusting with silica. The emulsion is formed by :

a) dispersing the starch matrix in water at room temp. in a 1:2 ratio. It is preferred that the starch is pregelatinised so that the emulsion can be carried out at this temperature. This in turn minimises perfume loss. There must be a "low viscosity" starch to achieve high starch concentrations in water and high perfume loadings.

b) the perfume oil is then added to the above mixture in the ratio of 0.8-1.05 : 1: 2, and the mixture is then emulsified using a high shear mixer. The shearing motion must produce oil droplets below 1 micron and the emulsion must be stable in this form for at least 20 mins (the function of the starch is to stabilise the emulsion once its mechanically made).

c) the mixture is spray-dried in a co-current tower fitted with a spinning disk atomiser. The drying air inlet temperature is low 150-200°C. This type of spray-drying ensures minimum loss of perfume and high drying rate. The granules have a particulate size of 50-150 microns.

d) the resulting dried encapsulates can contain up to 5% unencapsulated oil at the surface of the granules. To

improve the flow characteristics up to 2% hydrophobic silica can be optionally added to the encapsulates via a ribbon blender.

It may be desirable to add additional perfume to the composition, as is, without protection via the capsules. Such perfume loading would allow for aesthetically pleasing fragrance of the composition itself. Upon opening the package containing the composition and as the product is added to water, this immediate release of fragrance may be desirable.

This perfume would be added via conventional means, e.g., mixing, as is, into a liquid composition or spraying onto dry product compositions.

The laundry additive according to the composition of the present invention can be incorporated into a wide variety of compositions which deliver a perfume to a fabric including detergent and rinse added compositions.

Typically, for laundry detergent compositions an amount of the perfume particles is incorporated in the composition so as to provide the composition with from about 0.001% to about 10%, preferably from 0.1% to 3% perfume. The modified polyesters will be present in the detergent compositions from 0.1% to 10%, preferably from 0.1% to 5% by weight of the total detergent composition.

Furthermore, it has been found that the combined use of the encapsulated perfumes with modified polyesters and a clay softening system provide softening-through-the-wash compositions having both excellent cleaning and softening benefits performance while still maintaining a desirable perfume impact onto the fabrics, as well as maintaining the essential character of the perfume.

The clay softening system hereof will comprise a fabric softening clay present in an amount of at least 0.5%,

preferable from 4% to 30% by weight of the detergent composition. The preferred clays are of the smectite type.

Smectite type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq./100g.

Smectite clays can be described as three-layer expandable materials, consisting of aluminosilicates or magnesium silicates.

There are two distinct classes of smectite-type clays; in the first, aluminium oxide is present in the silicate crystal lattice, in the second class of smectites, magnesium oxide is present in the silicate crystal lattice.

The general formulas of these smectites are  $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$  and  $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ , for the aluminium and magnesium oxide type clay, respectively. The range of the water of hydration can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , as well as  $\text{H}^+$  can be co-present in the water of hydration to provide electrical neutrality.

It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in equilibrium exchange reactions with cations present in aqueous solutions. In such equilibrium reactions, one equivalent weight of solution cation replaces an equivalent of sodium, for example, and it is customary to measure clay cation exchange capacity in terms of milliequivalents per 100g. of clay (meq/100g.).

The cation exchange capacity of clays can be measured in several ways, including electrodialysis, by exchange with

ammonium ion followed by titration, or by a methylene blue procedure, all as set forth in Grimshaw, The Chemistry and Physics of Clays, Interscience Publishers, Inc. pp. 264-265 (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ionexchange capacity somewhere in the lower portion of the range, ca. 26 meq/100 g. for an average illite clay.

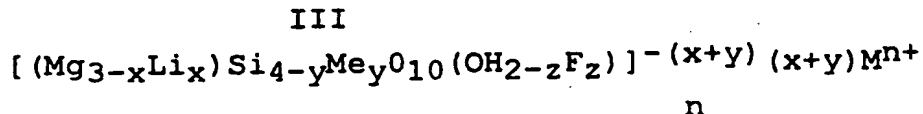
It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed such illite and kaolinite clays constitute a major component of clay soils. However, smectites, such as nontronite having an ionexchange capacity of approximately 50 meq/100 g.; saponite, which has an ion exchange capacity greater than 70 meq/100g., have been found to be useful fabric softeners.

The smectite clays commonly used for this purpose herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "fooler clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel #1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co. Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH 450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and tradenames can comprise mixtures of the

various discrete mineral entitites. Such mixtures of the smectite minerals are suitable for use herein.

Preferred for use herein are the montmorillonite clays.

Quite suitable are hectorites of natural origin, in the form of particles having the general formula



wherein  $\text{Me}^{\text{III}}$  is Al, Fe, or B; or  $y=0$ ;  $\text{M}^{\text{n}+}$  is a monovalent ( $n=1$ ) or divalent ( $n=2$ ) metal ion, for example selected from Na, K, Mg, Ca, Sr.

In the above formula, the value of  $(x+y)$  is the layer charge of the hectorite clay.

Such hectorite clays are preferably selected on the basis of their layer charge properties, i.e. at least 50% is in the range of from 0.23 to 0.31.

More suitable are hectorite clays of natural origin having a layer charge distribution such that at least 65% is in the range of from 0.23 to 0.31.

The hectorite clays suitable in the present composition should preferably be sodium clays, for better softening activity.

Sodium clays are either naturally occurring, or are naturally-occurring calcium-clays which have been treated so as to convert them to sodium-clays. If calcium-clays are used in the present compositions, a salt of sodium can be added to the compositions in order to convert the calcium clay to a sodium clay. Preferably, such a salt is sodium carbonate,



typically added at levels of up to 5% of the total amount of clay.

Examples of hectorite clays suitable for the present compositions include Bentone EW and Macaloid, from NL Chemicals, N.J., U.S.A., and hectorites from Industrial Mineral Ventures.

The clay softening system herein can comprise clay-flocculating agents. The compositions herein may comprise, from 0.05% to 20% by weight of the clay, of flocculating agent, if its molecular weight is 150,000-800,000 and from 0.005% to 2%, by weight of the clay, if its molecular weight is from 800,000 to 5 million. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. For proper interaction with the clay particles, the polymers should be fairly long chain, i.e., have a weight average molecular weight of at least 100,000. For sufficient water-solubility the weight average molecular weight of the polymers should not exceed 10 million. Most preferred are polymers having a weight average molecular weight of from 150,000 to 5 million.

The organic humectant optionally employed in the clay agglomerates herein, may be any of the various water soluble materials utilized for such a purpose. The organic humectant is preferably selected from the group consisting of a) aliphatic hydrocarbon polyols having from 2 to 9 carbon atoms; b) ether alcohols derived from the polyols of a); c) ester alcohols derived from the polyols of a); d) mono- and oligosaccharides; and mixtures thereof.

Highly preferred humectants include glycerol, ethylene glycol, propylene glycol and the dimers and trimers of glycerol, of ethylene glycol and of propylene glycol.

The clay softening system can comprise from 0.5% to 30%, preferably from 2% to 15%, of the humectant by weight of the clay.

### DETERGENT ADJUNCTS

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

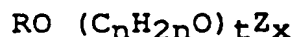
Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C<sub>12</sub>-C<sub>18</sub> fatty source preferably from a C<sub>16</sub>-C<sub>18</sub> fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. Examples of preferred alkyl sulphates herein are tallow alkyl sulphate, coconut alkyl sulphate, and C<sub>14</sub>-15 alkyl sulphates. The cation in each instance is again an alkali metal cation, preferably sodium.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average

hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

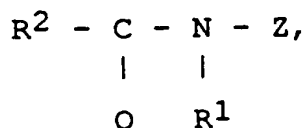
Especially preferred nonionic surfactants of this type are the C<sub>9</sub>-C<sub>15</sub> primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C<sub>14</sub>-C<sub>15</sub> primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C<sub>12</sub>-C<sub>14</sub> primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



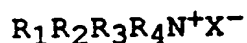
wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a

linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably,  $R^1$  is methyl,  $R^2$  is a straight  $C_{11-15}$  alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction. Suitable cationic surfactants include the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein  $R_1$  is  $C_8-C_{16}$  alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently  $C_1-C_4$  alkyl,  $C_1-C_4$  hydroxy alkyl, benzyl, and  $-(C_2H_4O)_xH$  where x has a value from 2 to 5, and X is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl. The preferred alkyl chain length for  $R_1$  is  $C_{12}-C_{15}$  particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for  $R_2R_3$  and  $R_4$  are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds for use herein are

- coconut trimethyl ammonium bromide,
- coconut methyl dihydroxyethyl ammonium bromide,
- decyl triethyl ammonium chloride or bromide,
- decyl dimethyl hydroxyethyl ammonium chloride,
- myristyl trimethyl ammonium methyl sulphate,
- lauryl dimethyl benzyl ammonium bromide,
- lauryl methyl (ethenoxy)<sub>4</sub> ammonium bromide.

The water-soluble cationic component of the compositions of the present invention is capable of existing in cationic form in a 0.1% aqueous solution at pH 10.

The water-soluble cationic compounds will normally be present in an amount of from 0.2% to 10% by weight of the detergent composition.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopoly-phosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ).

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula  $\text{R}-\text{CH}(\text{COOH})\text{CH}_2(\text{COOH})$  wherein R is C10-20 alkyl or alkenyl, preferably C12-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps.

Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates. The compositions according to the present invention may further comprise a bleach agent.

Any particulate inorganic perhydrate bleach can be used, in an amount of from 3% to 40% by weight, more preferably from 8% to 25% by weight and most preferably from 12% to 20% by weight of the compositions. Preferred examples of such bleaches are sodium perborate monohydrate and tetrahydrate, percarbonate, and mixtures thereof.

Another preferred separately mixed ingredient is a peroxy carboxylic acid bleach precursor, commonly referred to as a bleach activator, which is preferably added in a prilled or agglomerated form in granular detergents. Examples of suitable compounds of this type are disclosed in British Patent Nos. 1586769 and 2143231 and a method for their formation into a prilled form is described in European Published Patent Application No. 0 062 523. Preferred examples of such compounds are tetracetyl ethylene diamine and sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate.

Bleach activators are normally employed at levels of from 0.5% to 10% by weight, more frequently from 1% to 8% and preferably from 2% to 6% by weight of the composition.

Enzymes such as proteases, lipases, cellulase or amylases are particularly desirable ingredients of the compositions herein.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methyl-cellulose, carboxymethylcellulose and hydroxyethyl-cellulose, homo- or copolymeric polycarboxylic acids or their salts and polyamino compound. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers disclosed in detail in EPA 137 669, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. Polyamino compound such as those derived from aspartic acid are disclosed in EPA 305 282, EPA 305 283, and EPA 351 629.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4<sup>1</sup>-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino) stilbene-2:2<sup>1</sup> disulphonate, disodium 4, - 4<sup>1</sup>-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2<sup>1</sup> - disulphonate, disodium 4,4<sup>1</sup>- bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2<sup>1</sup>-disulphonate, monosodium 4<sup>1</sup>, 4<sup>11</sup> -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene 2-sulphonate, disodium 4,4<sup>1</sup> -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2<sup>1</sup> - disulphonate, disodium 4,4<sup>1</sup> -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2<sup>1</sup> disulphonate, disodium 4,4<sup>1</sup>bis (2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2<sup>1</sup>disulphonate and sodium 2(stilbyl-4<sup>11</sup>-(naphtho-1<sup>1</sup>, 2<sup>1</sup>:4,5)-1,2,3 -triazole-2<sup>11</sup>-sulphonate.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and

xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m<sup>2</sup>/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200 000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight. The incorporation of the suds modifiers is preferably made as separate particulates, and this permits the inclusion therein of other suds controlling materials such as C20-C24 fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene oxide which would otherwise adversely



affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3 933 672.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other components used in detergent compositions may be employed, such as suds boosting and stabilizers or activators therefore, soil-suspending agents, soil-release agents, pigments, photo-bleach activators, abrasives, bactericides, tarnish inhibitors and coloring agents.

The detergent compositions according to the invention can be in liquid, paste or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present

invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process and compositions of the invention can also be used as additive during laundry operations.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

EXAMPLE I (A/B/C/D/E)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

% by weight of the total detergent composition

|  | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> |
|--|----------|----------|----------|----------|----------|
| Linear alkyl benzene sulphonate                        | 8.0      | -        | -        | -        | -        |
| Polyhydroxy fatty acid amide                           | -        | 10       | -        | -        | -        |
| Alkyl alkoxyated sulfate                               | -        | -        | 9        | 9        | 9        |
| Tallow alkyl sulphate                                  | 1.80     | 1.80     | 1.80     | 1.80     | 1.80     |
| C <sub>45</sub> alkyl sulphate                         | -        | 3.00     | 3.00     | 3.00     | 3.00     |
| C <sub>45</sub> alcohol 7 times ethoxylate             | 1.3      | 4.00     | 4.00     | 4.00     | 4.00     |
| Tallow alcohol 11 times ethoxylated                    | 1.80     | 1.80     | 1.80     | 1.80     | 1.80     |
| C12-C14 dimethyl<br>(hydro- ethyl ammonium chloride)   | 2        | 2        | 1        | 2        | 1        |
| Dispersant   | 0.07     | 0.07     | 0.07     | 0.07     | 0.07     |
| Sud suppressor   | 1.5.     | 1.50     | 1.50     | 1.50     | 1.50     |
| Trisodium citrate                                      | 14.00    | 14.00    | 14.00    | 14.00    | 14.00    |
| Citric acid  | 3.00     | 3.00     | 3.00     | 3.00     | 3.00     |
| Zeolite  | 20.00    | 32.50    | 32.50    | 32.50    | 32.50    |
| Diethylenetriamine pentan-<br>ethylene phosphonic acid | 0.6      | 0.6      | 0.6      | 0.6      | 0.6      |
| Maleic acid acrylic acid<br>copolymer                  | 5.00     | 5.00     | 5.00     | 5.00     | 5.00     |
| Carboxymethylcellulose                                 | 0.2      | 0.2      | 0.2      | 0.2      | 0.2      |
| Cellulase (Endo-A)                                     | 0.03     | 0.03     | 0.03     | 0.03     | 0.03     |
| Savinase   | 0.60     | 0.60     | 0.60     | 0.60     | 0.60     |
| Lipolase   | 0.36     | 0.36     | 0.36     | 0.36     | 0.36     |
| Sodium silicate  | 2.00     | 2.00     | 2.00     | 2.00     | 2.00     |
| Sodium sulphate  | 3.50     | 3.50     | 3.50     | 3.50     | 3.50     |
| Percarbonate   | -        | -        | -        | 20       | 20       |
| Perborate  | 15       | 15       | 15       | -        | -        |
| TAED   | 5        | -        | 5        | -        | 5        |
| Soil release polymer                                   | 0.3      | 0.3      | 0.3      | 0.3      | 0.3      |
| Clay   | 12       | 12       | 12       | 12       | 12       |

|  | 25   |     |           |     |     |
|--|------|-----|-----------|-----|-----|
| Perfume  | 0.4  | 0.4 | 0.4       | 0.4 | 0.4 |
| Perfume Encapsulated   | 0.4  | 0.4 | 0.4       | 0.4 | 0.4 |
| Disodium-4,4'-bis (2-morpholino<br>-4-anilino-s-triazin-6-ylamino)<br>stilbene-2,2'-disulphonate | 0.25 | 0.2 | -         | 0.2 | 0.2 |
| Disodium-4,4'-bis (2-sulfostyryl)<br>biphenyl  | 0.25 | -   | 0.2       | -   | -   |
| Minors   |      |     | up to 100 |     |     |

Suds suppressor : agglomerate comprising 11% by weight of the component of polydimethylsiloxane, 14% TAE80 , 5% of C12-C22 hydrogenated fatty acids and 70% starch.

The soil release polymer in Examples A to E is a modified polyester being a random copolymer of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1,2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of monoesters of ethylene glycol and/or propane diol.

It is spray dried to form a granular product which is dry added, along with the perfume encapsulates, to the rest of the detergent composition.

#### Example F

A perfume encapsulate having the following composition was made :

|                               |               |
|-------------------------------|---------------|
| Perfume Oil                   | 47% by weight |
| Modified Starch (Narlex ST ®) | 50% by weight |
| Water                         | 2% by weight  |
| Hydrophobic silica            | 1% by weight  |

CLAIMS

1. A laundry detergent composition or component comprising :  
A) encapsulated perfume; and  
B) modified polyester;

said modified polyester being a substantially linear end-capped ester having a molecular weight ranging from about 500 to about 20,000; said ester consisting essentially of, on a molar basis :

- i) from about 1 to about 2 moles of two or more types of end-capping units selected from the group consisting of :
- a) ethoxylated or propoxylated hydroxy-ethane and propeanesulfonate end-capping units of the formula  $(\text{MO}_3\text{S})(\text{CH}_2)_m(\text{CH}_2\text{CH}_2\text{O})(\text{RO})_n-$ , wherein M is a salt-forming cation such as sodium or tetraalkylammonium, R is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 0 to 4;
  - b) sulfoaroyl units of the formula  $-(\text{O})\text{C}(\text{C}_6\text{H}_4)(\text{SO}_3\text{M})$ , wherein M is a salt forming cation;
  - c) modified poly(oxyethylene)oxy monoalkyl ether units of the formula  $\text{XO}(\text{CH}_2\text{CH}_2\text{O})_k-$ , wherein X contains from about 1 to about 4 carbon atoms and k is from about 1 to 100; and
  - d) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula  $\text{NaO}_3\text{S}(\text{C}_6\text{H}_4)-(\text{RO})_n-$ , wherein n is from 1 to 5 and R is ethylene or propylene or a mixture thereof;
- ii) from about 0.5 to about 66 moles of units selected from the group consisting of :
- a) oxyethyleneoxy units;
  - b) oxy-1,2-propyleneoxy units; and
  - c) mixtures of a) and b);

- iii) from about 1.5 to about 40 moles of terephthaloyl units; and optionally
  - iv) from 0 to about 26 moles of 5-sulfoisophthaloyl units of the formula  $-(O)C(C_6H_3)(SO_3M)C(O)-$ , wherein M is a salt forming cation such as an alkali metal or tetraalkylammonium ion.
2. A laundry detergent composition or component according to Claim 1, said modified polyester being a random co-polymer of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulfobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol.
  3. A laundry detergent composition or component according to either claim 1 or 2, wherein the encapsulated perfume comprises an encapsulating material which is a water-soluble or water-dispersible material.
  4. A laundry detergent composition or component according to claim 3, wherein the encapsulating material is a composition of polysaccharide and polyhydroxy compound.
  5. A detergent composition or component according to claim 1, wherein the encapsulated perfume comprises an encapsulating material which is a water insoluble material.
  6. A laundry detergent composition according to claim 1 further comprising :
    - C) a softening clay.
  7. A rinse added composition according to claim 1 to 4.

## INTERNATIONAL SEARCH REPORT

In. .tional application No.  
PCT/US94/02080

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C11D 3/50, 3/37  
US CL :252/174.11, 174.13, 174.21, 174.23, 174.24, DIG. 15  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/174.11, 174.13, 174.21, 174.23, 174.24, DIG. 15

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS:perfume(1p) (encapsul? or coat?), dimethyl terephthalate, ethylene glycol,propane diol

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--|-----------------------|
| Y         | US, A, 4,976,879 (MALDONADO ET AL) 11 DECEMBER 1990. SEE COLS. 4-10, COL 31, LINE 24.  | 1-6                   |
| Y         | US, A, 4,863,619 (BORCHER ET AL) 05 SEPTEMBER 1989. SEE COL. 6, LINE 44, COL 11, LINE 68, COL. 23, LINE 65-COL. 24, LINE 12. | 1-6                   |
| P, Y      | US, A, 5,256,168 (MORRALL ETAL) 26 OCTOBER 1993. SEE COL. 2, LINE 38, COL. 6, LINE 45, COL. 24, LINE 5.                      | 1-6                   |
| P,Y       | US, A, 5,196,133 (LESLIE ET AL) 23 MARCH 1993. SEE COL. 2, LINE 37, COL. 6, LINE 44, COL. 23, LINE 55.                       | 1-6                   |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

|   |  |
|---|--|
| * Special categories of cited documents:  | *T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention   |
| *A* document defining the general state of the art which is not considered to be of particular relevance  | *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone   |
| *E* earlier document published on or after the international filing date  | *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *Z* document member of the same patent family  |
| *O* document referring to an oral disclosure, use, exhibition or other means  |  |
| *P* document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

06 MAY 1994

Date of mailing of the international search report

MAY 31 1994

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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**INTERNATIONAL SEARCH REPORT**Int. l. application No.  
PCT/US94/02080**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y         | GB, 1,464,616 (POLAK) 16 FEBRUARY 1977. SEE COL. 3, LINES 30-115.                  | 1, 3, 4               |
| Y         | US, A, 4,234,627 (SCHILLING) 18 NOVEMBER 1990. SEE COL. 3, LINE 60-68.             | 1-5                   |
| Y         | US, A, 3,455,838 (MAROTTA ET AL) 15 JULY 1969. SEE COL. 2, LINE 54-71.             | 4                     |



# INTERNATIONAL SEARCH REPORT

Inte. tional application No.  
PCT/US94/02080

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.